Research Strategy for Oxygenates in Water

WORKSHOP REVIEW DRAFT

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT

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1. INTRODUCTION

The contamination of ground and surface waters by motor vehicle fuels and fuel additives is not a new problem, given the pervasive distribution and use of fuels. Well over a million underground fuel storage tanks exist in the United States, and leaks from these tanks have been the focus of major programs to prevent or remediate such releases. Transport of fuels via pipelines and in bulk containers also presents the potential for accidental releases and consequent environmental contamination. Experience suggests that contamination from these and other sources of fuel releases can affect water quality and the biota that depend upon the water, including human populations that may use the contaminated water.

Against this baseline of experience with fuel-related contamination of ground and surface waters, recent events have focused attention on what appear to be somewhat different characteristics associated with fuels containing chemicals known as oxygenates. Oxygenates are added to fuel to increase its oxygen content and thereby reduce certain emissions from combustion of the fuel. Of the several ethers and alcohols that may serve as oxygenates, methyl tertiary butyl ether (MTBE) is the most commonly used. Monitoring of groundwater quality by the U.S. Geological Survey (USGS) indicates that MTBE has become detectable in shallow groundwater samples in certain urban areas in recent years, with concentrations ranging from below the reporting level of 0.2 µg/L to over 20,000 µg/L (Squillace et al., 1996). Reports of point-source MTBE contamination of drinking water sources at well over 100 µg/L, including aquifers serving as the primary source of drinking water for the city of Santa Monica, CA (California Department of Health Services, 1997), raise several important questions about the assessment and management of potential environmental and public health impacts of oxygenated fuels.

A key question is whether oxygenates in water pose a threat to human health or the environment. To assess the risks of MTBE or any other oxygenate, the potential for exposure to, and effects of, the contaminant(s) in question must be characterized. At present, however, only limited information exists for assessing the possible risks of oxygenates in water. For example, the extent of population exposures to MTBE in drinking water is unknown. Even in cases where MTBE is clearly present in public or private water supplies, limited guidance exists as to the levels that would be acceptable or unacceptable from a public health or aesthetics standpoint. In 1992, EPA's Office of Water released a draft Health Advisory for MTBE in drinking water. The

draft document identified a lifetime Health Advisory level of 200 µg/L, but noted that the level would probably be lowered to 20 µg/L to account for its possible carcinogenic potential. A final Health Advisory for MTBE has not been issued to date, in large part due to limitations in the health effects database for MTBE by the oral route of exposure. The uncertainties in assessing the health risks of MTBE are reflected somewhat in the various guidance values (i.e., advisories, action levels, standards) issued by individual states, which range from 35 µg/L in California to 230 µg/L in Illinois (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). In addition to the health risk issue is the "aesthetic" issue of the unpleasant taste and odor of MTBE and other oxygenates and the problem of determining what contaminant concentration is acceptable to water consumers.

Other key questions concern the actions that might be taken to address oxygenate contamination of water, given a judgment that a problem exists. For example, what are the sources of contamination?, how long is the contamination likely to persist?, how widespread might the contamination be?, what cost-effective technological methods exist to remove the contaminant(s) from water?, how can further contamination be avoided?, and a host of other questions face risk managers. A recent review of fuel oxygenates and water quality (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) notes that for various reasons, including the potentially greater persistence of MTBE in groundwater than other components of gasoline, remediation of MTBE-contaminated groundwater may pose unique problems. The Interagency Assessment also notes the possibility that ground water could be contaminated by oxygenates in the ambient atmosphere. A quantitative answer to the question of whether non-point sources or point sources, such as leaking underground storage tanks, pose a greater potential risk of environmental contamination is not available at present.

Risk assessment and risk management require information, which is generally obtained through research, data collection, or analysis of data that may already exist. The purpose of this document is to identify key issues related to oxygenates in water and describe a strategy for obtaining information to address these issues. This research strategy builds on and extends an earlier document, *Oxyfuels Information Needs* (U.S. Environmental Protection Agency, 1996), which encompassed water issues but tended to emphasize human health inhalation risk issues. As noted in the 1996 information needs document, the benefits and risks of any given oxygenate must be assessed in relation to an alternative, such as conventional gasoline. A full comparative

assessment of this type is obviously a complex, multi-faceted endeavor. The present research strategy is much more limited in scope. This strategy document is primarily intended to serve as a starting point and general guide to planning research related to oxygenates in water; it does not attempt to lay out in detail the specific studies and projects that may be needed. Nor is this document a formal assessment of environmental or health risks associated with oxygenates or an in-depth analysis of candidate risk management options for addressing this problem. The reader may wish to consult other reports for more in-depth evaluations of available information on the health and environmental effects of oxygenates (e.g., U.S. Environmental Protection Agency, 1993, 1994; Health Effects Institute, 1996; Interagency Oxygenated Fuels Assessment Steering Committee, 1996, 1997; National Research Council, 1996), especially the "Water Quality" chapter from the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). Note that all of these reports have pointed out the lack of adequate information by which to assess fully and definitively the risks and benefits associated with oxyfuels in comparison to conventional fuels.

Some brief background information on why fuel oxygenates exist may be appropriate. The 1990 Clean Air Act Amendments (CAAA) created two fuel programs to be administered by the U.S. Environmental Protection Agency (EPA) that require the use of oxygenates. The first program began in the fall of 1992 with the objective of reducing carbon monoxide (CO) emissions in several areas of the country where the National Ambient Air Quality Standard (NAAQS) for CO was exceeded. Under this program, the CAAA required the sale of gasoline with an oxygen content of 2.7% by weight during the winter or cold weather season in designated areas that failed to attain the NAAQS for CO. The second program required the year-round use of reformulated gasoline containing 2.0% oxygen by weight, beginning in 1995, in selected areas having the highest levels of ozone. In addition to reducing emissions of ozone precursors, the reformulated gasoline (RFG) program was also intended to help reduce the emissions of certain toxic organic air pollutants. Collectively, cold-weather oxygenated gasoline and year-round reformulated gasoline may be referred to as "oxyfuels."

Although MTBE and, to a lesser extent, ethanol (EtOH) currently dominate the marketplace, no specific oxygenate is required or designated by the 1990 CAAA. Several other ethers and alcohols may also serve as oxygenates and could become more prevalent, depending on various factors such as cost, ease of production and transfer, and blending characteristics.

Other possible oxygenates include ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), tertiary amyl ethyl ether (TAEE), diisopropyl ether (DIPE), dimethyl ether (DME), and tertiary butyl alcohol (TBA). To achieve the specified oxygen content requirements, approximately 15%-vol MTBE or 7.5%-vol EtOH can be used to yield the 2.7%-wt oxygen for the winter fuel program and approximately 11%-vol MTBE or 5.5%-vol EtOH for the 2.0%-wt oxygen required by the RFG fuel program. According to EPA's Office of Mobile Sources, roughly 30% of U.S. gasoline currently contains some form of oxygenate for air quality improvement purposes. Approximately an equal proportion of U.S. fuel contains MTBE or EtOH as an octane-enhancer for gasoline, a practice that began in the late 1970s in the United States as lead was phased out. The concentration of MTBE used for octane purposes in conventional gasoline may vary widely up to an allowable limit of 15%-vol MTBE, depending on other constituents and properties of the fuel, but probably is more typically on the order of 6 to 8%-vol MTBE. Gasoline containing 10% EtOH, often referred to as "gasohol," represents about 10% of all gasoline sold in the U.S., but may be much more prevalent in certain locales, particularly in the Midwest. Approximately 21 billion kg MTBE was used in U.S. gasoline in 1995 and fuel ethanol use was about 3.8 billion kg (U.S. Department of Energy, 1995a, b).

This document applies to all ether and alcohol oxygenates unless otherwise stated. It tends to focus on MTBE in part because of its predominant use and in part because more information may be available on MTBE than the other ethers and alcohols (except perhaps for EtOH). Nevertheless, it should not be inferred that the only oxygenate warranting attention is MTBE. The chemical properties of several oxygenates are listed in Appendix 1.

This research strategy is organized around the following headings.

- Occurrence
- Source Characterization
- Materials Compatibility
- Transport
- Transformation
- Contaminant Removal
- Exposure
- Aquatic Toxicity
- Health Effects

Within each of these areas, a brief background section highlights currently available information on key issues, followed by a section that identifies research or other information gaps that emerge as needs. Note that the grouping of topics is somewhat arbitrary. The overlap in various areas should be seen as a potential benefit in terms of combining objectives and resources for projects that can be feasibly and appropriately linked. Such leveraging of resources should extend across organizational boundaries as well.

2. OCCURRENCE

2.1   Background

MTBE was the second most frequently detected volatile organic compound (VOC) in shallow groundwater from selected urban areas monitored under the National Water Quality Assessment (NAWQA) program of the USGS during 1993 and 1994 (Squillace et al., 1996). Of 210 sampled wells and springs, 56 (27%) contained MTBE (28% contained chloroform; 5% contained benzene). Sixty wells and one spring contained MTBE or BTEX; 79% had MTBE alone, and 13% had both MTBE and BTEX. Of the total urban well and springs sampled, 3% exceeded 20 μg/L. In another study by the USGS (Delzer et al., 1996), MTBE was found to be the seventh most frequently detected VOC in municipal storm water. Limited data collected by EPA regional offices for the "Water Quality" chapter in the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) indicated that 51 public water suppliers have detected MTBE (out of seven states that responded). Although not statistically representative, these data suggest that MTBE occurrence is not necessarily limited to ground water. Other regional studies of MTBE occurrence are ongoing in California surface waters (Dale et al., 1997), New England aquifers (Grady, 1997), aquifers and surface waters of Long Island, New York and in New Jersey (Stackelberg et al., 1997), and fractured bedrock aquifers in Pennsylvania (Lindsey et al., 1997). Since February 1997, the California Department of Health Services has required public water suppliers to monitor their drinking water sources (i.e., wells and surface water bodies) for MTBE. To date, over 2,000 drinking water sources in California had been sampled for MTBE contamination. Of these, 26 sources (1.2 %) had detectable levels of MTBE, including five sources with samples

exceeding California's drinking water interim action level of 35 µg/L (California Department of Health Services, 1997).

USGS and EPA have entered into a cooperative agreement to conduct a pilot study in 12 New England and mid-Atlantic states where MTBE has been extensively used as a gasoline additive. The pilot project will describe the occurrence and distribution of MTBE and other VOC's in ground water and the extent of potential human exposure to these compounds from ground-water derived drinking-water supplies. Project tasks include: (1) compilation, review, analysis, and publication of information on VOC concentrations in wells sampled for the NAWQA program and other USGS studies in New England and mid-Atlantic states; and (2) development of a computer database of VOC concentrations in drinking water at the tap (if available) and in ground water withdrawals from drinking water supplies (at the well head) assembled from data maintained by state or local health agencies and water utilities that conduct VOC monitoring of public or private drinking water supplies in the region. The project will be managed under the general direction of the USGS National Synthesis Program.

Existing data sets are too limited in scope to estimate the prevalence and degree of contamination of groundwater, surface water, or drinking water in the United States, and it is not clear that current studies being conducted in different regions of the country will provide a comprehensive and representative sampling of oxygenate impacts on water quality for the entire nation. Without adequate information of this type, it will be difficult to assess the scope of the problem and determine appropriate measures to address it or evaluate the effectiveness of such measures.

To require monitoring of drinking water for an unregulated contaminant such as MTBE or other oxygenates, EPA must first promulgate regulations requiring the collection of the data, with monitoring schedules based on the size of the public water system. Under 1996 amendments to the SDWA, EPA is required to issue by February 1998 a list of unregulated contaminants, the "candidate contaminant list," that may be subject to more extensive evaluation for occurrence and/or health impacts. A draft of the list, which is scheduled for release in September 1997, includes MTBE. If it remains on the final list scheduled to be issued in February 1998, it will be evaluated for possible inclusion on a list of unregulated contaminants that would be subject to required monitoring by the states. The latter list must be finalized by August 1999.

According to a draft background document on "Options for the National Drinking Water Contaminant Occurrence Data Base" (U.S. Environmental Protection Agency, 1997), MTBE is proposed for inclusion in such a database. If EPA's Office of Water ultimately decides to promulgate rulemaking that requires monitoring of one or more oxygenates, the data would go into the national occurrence database, which would be based on the Safe Drinking Water Information System (SDWIS). Again, the required collection of data on MTBE or other oxygenates is contingent upon a decision by EPA's Office of Water to require such monitoring, which remains to be determined.

The Clean Water Act, Section 305(b) requires that states and other participating jurisdictions submit water quality assessment reports every two years to EPA. Based on these reports, EPA prepares the National Water Quality Inventory Report to Congress. However, a state may or may not provide data on specific unregulated contaminants such as MTBE in 305(b) reports, depending on the individual state's water quality priorities.

2.2   Needs

As stated in the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) and affirmed by the NAS/NRC Review Committee (National Research Council, 1996), oxygenates should be added to existing VOC analyte schedules and as routine target analytes for VOCs in drinking water, waste water, surface water, groundwater, and remediation sites. Such monitoring is needed to support long term tracking of possible changes in water quality and population exposures. Although MTBE can be analyzed using standard purge-and-trap capillary column gas chromatography (U.S. Environmental Protection Agency, 1992), the use of a flame ionization detector is sensitive to all organic compounds and it is very difficult to separate the MTBE peak from the complicated petroleum fuel peaks. A photo ionization detector (PID) is not sensitive to alkanes. The use of this detector should be evaluated for the analysis of MTBE in water contaminated with gasoline or diesel fuel. Analytic methods for most of the other ethers and alcohols, as well as by-products, need to be identified and evaluated. Raman and infrared spectroscopy are techniques that provide compound-specific information, and fiber optic technology allows these spectral techniques to operate as remote sensors. Fiber optic biosensors have been developed for BTEX in gasoline as well as alcohols in general. These techniques need to be investigated and developed as

cost-effective field analytical methods. Protocols for sample collection and analysis for specific oxygenates in water should be examined for representativeness, accuracy, reproducibility, method detection limits (MDL), and practical quantitation limits (PQL). In addition, quality assurance and control requirements should be defined and laboratory certification criteria developed.

The Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) contains a recommendation that a national database for cataloging monitoring data should be developed cooperatively among relevant governmental and private organizations, to be administered by a single federal agency. At present, existing "national" databases appear to be limited in their respective scopes. EPA's SDWIS contains drinking water data from public water supply distribution systems, whereas the USGS National Water Inventory System (NWIS) database contains ambient water quality data. Assuming that oxygenates are added to VOC analyte monitoring lists, an effort should be made after a reasonable period (e.g., 5 years from now) to analyze these or other databases for trends in occurrence of oxygenates in water. These analyses should be linked to exposure assessment efforts (see Section 8) and evaluated for guidance as to whether more intensive monitoring or other actions are warranted.

To the extent possible, monitoring efforts and database designs should be undertaken in a manner to relate qualitatively and quantitatively to exposure assessments for human populations and aquatic biota (see Section 8).

3. SOURCE CHARACTERIZATION

3.1   Background

Releases of fuel oxygenates occur during manufacture, distribution, storage, and use, particularly from point sources such as underground storage tanks, pipelines and refueling facilities. The Toxics Release Inventory (TRI) estimates that MTBE production releases in the United States amounted to approximately 3.3 million pounds (1,500 metric tons) in 1994. Of this total, about 97% was released to the air and less than 3% was discharged to surface water. For mobile sources, assuming an estimated consumption of 21 billion kg MTBE in 1995 (based

on imported as well as domestic production volumes, U.S. Department of Energy, 1995a,b), and an average U.S. corporate fleet emission rate of approximately 3.8 mg MTBE per gram MTBE in fuels (Wyborny, 1997) total motor vehicle emissions of MTBE in 1995 are estimated to have been on the order of 80 million kg in the United States.

Oxygenates released to air degrade with a half-life as short as 3 days (Smith et al., 1991; Wallington et al., 1988). However, MTBE is soluble in water and partitions readily from air to precipitation. Additionally MTBE may partition even more readily into snowflakes, because they have a greater surface area than raindrops and MTBE has a higher water solubility at lower temperatures. This process could result in land surface and subsequent surface and groundwater contamination. The observed detection of MTBE in about 41 (7%) of 592 storm water samples collected in 16 cities and metropolitan areas from 1991 to 1995, with the highest percentage of detections found in samples collected during high MTBE usage winter months (Delzer et al., 1996), suggests a possible correlation with atmospheric washout of MTBE in rain or snow to the ground surface. The measured concentrations of MTBE ranged from 0.2 to 8.7 ppb, with a median of 1.5 ppb (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). Modeling calculations predicted MTBE concentrations in rainwater ranging from <1 ppb to 3 ppb, within the range of concentrations actually found in groundwater samples. The use of shallow groundwater for public as well as private water supplies makes such non-point contamination a potential public health issue as well as an environmental quality issue.

Direct releases of MTBE and other fuel oxygenates to surface and groundwater sources of drinking water may also occur. The majority of direct releases of MTBE to surface water reported to TRI were attributable to only a few petroleum product facilities. As for subsurface releases, according to EPA's Office of Underground Storage Tanks (USTs), approximately 1.1 million regulated USTs are currently in use at approximately 400,000 facilities in the United States. Not all of these USTs contain oxyfuels or gasoline with MTBE or ETOH as octane enhancers, but the percentage with or without oxygenate is unknown. Some of the earliest releases involving MTBE occurred in Maine in the mid-1980s (Garrett, 1987). More recently, drinking water wells in Santa Monica were shut down because of MTBE contamination. The source of the contamination is unclear, but one or more leaking USTs may be involved (Anonymous, 1996). Since 1988, there have been 330,000 confirmed releases from regulated USTs, and it is estimated that 100,000 further releases will be reported in the next few years as

existing USTs are replaced, upgraded, or closed. This estimate does not include an even greater number of federally unregulated storage tanks. Although EPA regulations (40 CFR 280.21) require that all USTs be upgraded, closed, or replaced by December 1998, current estimates indicate that 65 to 75% of USTs will be in compliance by that date.

Notwithstanding recent and ongoing studies, it is not clear what the major inputs of MTBE or other fuel oxygenates to groundwater are, i.e., what fraction of the MTBE or other oxygenate load is diffuse (e.g., from precipitation) or is related specifically to spills or leaks from contained material. Although relatively high groundwater concentrations may be readily associated with point source releases, concentrations on the order of 10 ppb or lower could be associated with non-point sources as well as point sources.

3.2   Needs

The relative loads or fluxes of the oxygenates to surface and groundwaters from point sources versus diffuse (non-point) sources must be more accurately determined. An obvious research need in this regard is the identification of a "source signature" for oxygenates that would permit reliable source identification and possibly even source apportionment when used in conjunction with fate models. For example, is it possible that upon extended storage MTBE or ETBE forms a unique polymer or condensation product in gasoline that is stable enough upon release to be used as a point source signature and tracer? Similarly, are there air pollutants or specific oxygenate photodegradation products that are scavenged with oxygenates in precipitation that could be used as an atmospheric source signature and tracer?

Another need is to construct and parameterize a model linking air to land to surface water and groundwater fate for oxygenates that can be used in sensitivity mode to conduct exposure assessments, design management and remediation strategies, and assist in source identification and apportionment. Such an airshed-watershed model, using the most recent MTBE air data for a northern city in the winter season, could be used to predict upper limit values of surface and groundwater concentrations from ambient sources that could be compared to measured values. An ongoing USGS study at Glassboro, NJ (Baehr and Ayers, 1997) may help address this need. In particular, the model could be used to estimate snow blanket buildup of oxygenates and subsequent release at first thaw. These model results could then be compared to data from a field study designed to test this potential pulse loading mechanism in a watershed. Once this

modeling tool is developed and tested, it could be used to provide a national estimate of ambient contributions to surface and shallow groundwater. It could also be used to provide point and non-point source aggregate concentrations within specific watersheds as a function of time (season) for total exposure assessment purposes.

4. MATERIALS COMPATIBILITY

4.1   Background

Fuel oxygenates are transported and stored in underground tanks and pipelines in blended gasoline or as neat (i.e., undiluted) product, and failures in any component of these systems may result in significant accidental releases of oxygenates or oxyfuels to the environment. Neat oxygenates can be very aggressive to elastomeric or polymeric materials (e.g., O-rings, gaskets) found in virtually all equipment used for storing and transporting these products. Neat MTBE has been observed to cause elastomers to swell and to compromise the integrity of valves, pumps, flanges, and control valves in pipelines (Westbrook and French, 1995; Alexander et al., 1994). Some of this work suggests that MTBE at <20% volume concentration in gasoline does not significantly swell elastomers after contact for a month. The American Petroleum Institute (1994) reported a survey of industry experience with oxygenated fuels and noted significant adverse effects on certain elastomers. Many industries are using new types of elastomers that are more compatible with oxygenates, but the long-term performance of older materials remains to be determined.

4.2   Needs

It is important to characterize fully the effects of ethers and alcohols on elastomers, fiberglass, and other components of pipelines and tanks, particularly after several years of aging. Based upon the results of these studies, new and improved approaches and technologies should be developed to: (1) enhance the speed and accuracy of detecting, locating, and assessing system problems; (2) repair and replace problem areas more efficiently and effectively; and (3) prevent future problems from occurring through innovative design concepts. It would be useful if manufacturers of these materials and equipment would provide any available data that they may

have already collected or are in the process of collecting. If such data are not available, testing should be initiated, particularly focusing on the compatibility of polymeric and elastomeric materials with ethers and alcohols and the compatibility of fiberglass with alcohols.

5. TRANSPORT

5.1   Background

Oxygenates may enter groundwater from diffuse sources, as would occur through dissolution from the atmosphere into rain or snow during precipitation events or from storm water runoff, or from dissolution of oxygenates in contact with groundwater flowing past point sources such as USTs or fuel spills. The transfer of MTBE from the unsaturated zone into the saturated zone is predicted by numerical modeling to occur rapidly during rainfall events (Pankow et al., 1997). However, no field observations of MTBE concentrations in groundwater during and after precipitation events are known to have been conducted.

The transport of oxygenates through aquifers, particularly MTBE, would be expected to be conservative; that is, it would be expected to travel at nearly the same velocity as the groundwater. In a mixed composition contaminant source, such as is found in oxygenated fuels, each individual component will travel at a rate dependent on its water solubility and sorption tendency for soil. MTBE is more soluble in water and less sorbed to soils than any of the "BTEX" compounds (benzene, toluene, ethylbenzene, xylenes). Given sufficient time and distance, each component will separate within the plume according to basic chromatographic principles. Consequently, over time, MTBE would be expected to be at the leading edge of the plume, or in the extreme case over a long period of time, MTBE could become completely separated from the rest of the plume if the original source was eliminated. If biodegradation of the oxygenate occurs (see Section 6), it will interact with the transport process such that the front may appear to recede or be stabilized.

Generally, aquifer vulnerability to oxygenate contamination can be predicted using current wellhead protection models (e.g., WhAEM, WHPA), which are being used on a case-by-case basis. The required parameters for these models are hydrologic, geologic, and contaminant-specific. The required chemical data for modeling oxygenate transport are

generally known, but again, transformation rates for the subsurface soil, vadose zone, and aquifers are required to run these models. The vulnerability of deep aquifers to oxygenate contamination is not well documented.

5.2   Needs

Given the progress made in the last several years on the hydrologic modeling of organic compounds, particularly the BTEX compounds, reasonable estimates of transport can be made for oxygenates, particularly MTBE. For instance, it is understood that MTBE would be expected to move at a higher flow rate than BTEX compounds because it is more water soluble and less attenuated by the solid matrix than the BTEX compounds. However, the impact that biodegradation will have on MTBE plume movement is less well understood. The greatest need, therefore, is to determine biodegradation rates for MTBE, other oxygenates, and their by-products under typical groundwater transport conditions, as outlined in the section on transformation below. Field studies need to be conducted to validate modeled rates of MTBE infiltration during precipitation events to determine the extent to which diffuse sources contribute to groundwater contamination. Three dimensional delineation of MTBE plume morphology in a variety of hydrological settings can be accomplished using push sampling techniques at multiple levels. Deep aquifer vulnerability should be examined by applying state-of-the-art fate models for scenarios that include areas that have high oxygenate use.

6. TRANSFORMATION

6.1   Background

Transformation processes include a variety of chemical, physical, or biological processes that reduce mass, toxicity, mobility, volume, or concentration of contaminants in soil and water. For surface water, potential transformation processes are biodegradation, photolysis, and hydrolysis. In groundwater, the potential transformation processes are biodegradation and hydrolysis. Knowledge of photolytic and hydrolytic processes is adequate. Photolysis is important for MTBE in surface water, but hydrolysis is not an important process for MTBE.

Data on the rates and pathways of MTBE biodegradation are inconclusive, and only a limited amount of work has been accomplished. Additionally, it is difficult to compare studies because they have been performed under a wide variety of experimental conditions. For instance, Sulflita and Mormile (1993) reported no biodegradation of MTBE in lab microcosms using sediments from a petroleum-contaminated site, whereas Salanitro et al. (1994) reported isolating a bacterial strain that degrades MTBE under specific lab environments. In another study, it was reported that MTBE was biodegraded when inoculated with a specific bacterial enrichment, but not when inoculated with activated sludge (Petroleum Environmental Research Forum, 1993). Mormile et al. (1994) observed limited biodegradation of MTBE in sediments, as did Borden et al. (1997). In an ongoing microcosm study using acclimated sediment from the Elizabeth City Coast Guard Base in North Carolina, rapid and extensive biodegradation of MTBE under methanogenic conditions has been observed (B. Wilson, U.S. Environmental Protection Agency, unpublished data). Marked reduction in the concentrations of MTBE and benzene following termination of active remediation of fuel contamination was also observed in another plume at the same U.S. Coast Guard base (Cho et al., 1997).

Products of MTBE biodegradation include TBA and tertiary butyl formate (TBF), as documented in a few studies (see Interagency Oxygenated Fuels Assessment Steering Committee, 1997). However, comprehensive identification of biodegradation products and reaction pathways has not been undertaken. Natural or intrinsic bioremediation is being widely accepted as either a primary or "polishing" process for groundwater remediation. Rapid transport, coupled with a slow rate of biodegradation, if confirmed, could compromise the validity of this remediation strategy for MTBE.

6.2   Needs

Biodegradation rates and pathways for MTBE and other oxygenates need to be measured experimentally to understand and predict the fate of these compounds in the environment, and to design cost-effective removal and remediation technologies. Additional field-scale studies on the biodegradation of MTBE and other oxygenates need to be conducted. Microcosm studies using well characterized sediments and aquifer materials from a wide variety of sources and under a matrix of geochemical conditions are needed. The geochemical conditions should include a range of redox and pH conditions and several dissolved electron receptors (e.g., oxygen, nitrate,

sulfate) common in contaminated groundwater systems to determine the importance of aerobic and anaerobic reactions in MTBE degradation. Transformation products need to be identified and quantified so that specific biochemical pathways under different geochemical conditions can be determined. Field studies need to be designed and conducted in tandem with microcosm studies for validation purposes. The rates of biodegradation will be key in understanding the fate of oxygenates in the subsurface, in developing in-situ and ex-situ contaminant treatments, in implementing natural attenuation protocols, and in conducting aquifer vulnerability modeling. Identification of by-products and characterization of their environmental fate is needed to develop a complete picture of the effects of oxygenates on the environment.

7. CONTAMINANT REMOVAL

7.1   Background

Various technologies are available for removing contaminants from soils, groundwater, and drinking water. The following discussion is not meant to differentiate these processes in their applications, but rather to address generally the efficiency of these technologies for soils or water contaminated with MTBE or other oxygenates.

Soil vapor extraction (SVE) is commonly used to remove gasoline contaminants from the unsaturated zone at spill sites. Based on its high vapor pressure and low affinity for organic carbon in soil, MTBE would be expected to be readily removed from soil by vapor extraction. A computer model, VENT2D, has been used to simulate this process for a gasoline-MTBE mixture (Benson, 1994). In this simulation, MTBE showed the highest rate of mass loss of five gasoline components, as would be predicted based on their relative vapor pressures. Hence, MTBE and other ethers with high vapor pressures are not expected to be problematic for this technology. Low-temperature thermal desorption (LTTD) is an ex situ soil treatment technology that uses temperatures below ignition levels to separate volatile contaminants from soil. Due to MTBE's high vapor pressure, both SVE and LTTD are very effective in removing MTBE from soil. However, because MTBE separates from gasoline and dissolves quickly in water, SVE and LTTD must be used soon after a release; otherwise most of the MTBE may have already moved from the soil into the groundwater.

The efficiency of in-situ biological treatment for oxygenates is subject to debate. The feasibility of an in-situ bioremediation process will be dependent on the biodegradation rate, which, as noted throughout this document, remains to be investigated and characterized more fully.

Because MTBE does not adsorb well to soil and is highly soluble in water, "pump and treat" technology, i.e., pumping contaminated groundwater and treating it above ground, may be effective in conjunction with certain contaminant-removal processes for MTBE. Studies reported in the literature have indicated that MTBE biodegrades in ex-situ biological treatment systems under aerobic (Salanitro, 1994; Mo et al., 1996; Cowan and Park, 1996) and anaerobic (Sulflita and Mormile, 1993) conditions. The Petroleum Environmental Research Forum (1993) reported that MTBE biodegraded when inoculated with a specific bacterial enrichment, but not with activated sludge inoculum. However, the study with activated sludge inoculum was conducted for a 30-day period, which may have been insufficient for the bacterial population to acclimate to MTBE. Sufficient evidence exists that under some conditions MTBE is biodegradable. Once these conditions are fully defined, it is anticipated that ex-situ biological treatment technologies for MTBE biodegradation will be successful due to the ability to fully control the conditions of the ex situ system.

Granular activated carbon (GAC) adsorption and air stripping are the most commonly used treatment processes for organic contaminants. However, neither is very effective for removing MTBE because of the limited adsorption capacity of activated carbon for MTBE (Speth and Miltner, 1990). Therefore, it is not expected that adsorption would be generally used for removing MTBE on a large scale. This is especially true at high influent concentrations that would limit the time that a GAC column could be effective. For public water supplies, field studies have shown that carbon adsorption is not cost effective for MTBE removal unless the concentrations are very low (McKinnon and Dyksen, 1984). For example, with an influent concentration of 30 μg/L, the carbon beds needed to be regenerated frequently. Other ether oxygenates have slightly lower solubilities than MTBE, which indicates that their adsorption would be more effective. However, alcohol oxygenates such as EtOH and TBA are infinitely soluble, and thus adsorption would be ineffective for these compounds.

For volatile organic compounds, air stripping is a cost effective alternative. However, the Henry's constant for MTBE is very low, which indicates a relatively low efficiency for air

stripping. Air stripping at a very high air-to-water ratio (200) was found to be effective in removing 93% of MTBE (McKinnon and Dyksen, 1984). Lower air-to-water ratios were not effective. For DIPE, the percentage removal with air stripping was greater than 99%. In this study, the cost of the air stripping treatment was approximately 55% of that for the carbon treatment. However, the off gas of the air stripping unit was not treated, which would approximately double the cost of the air stripping system. Air stripping followed by GAC adsorption was found to be very effective for MTBE removal in this study, as was also found by Truong and Parmele (1992). Other oxygenates such as ETBE, TAME, and DIPE have higher Henry's constants than MTBE, which indicates that air stripping would be more effective for them. However, alcohol oxygenates have lower Henry's constants, indicating that air stripping would not be effective for these compounds.

Yeh (1992) found that hydrogen peroxide in the presence of iron (Fenton's reaction) degraded ETBE and MTBE. This was later confirmed by Chen et al. (1995) and other researchers under laboratory conditions. Therefore, the hydroxyl radicals produced by Fenton's reaction appear to be an effective treatment agent. Ozone, ozone/UV, and ozone/peroxide also have potential as treatment technologies for oxygenate destruction. Because these systems increase the biodegradability of the organic residues in the water, biofiltration may be recommended following oxidation to control for biodegradable residues. This would result in an effective two-stage process: abiotic oxidation followed by aerobic biodegradation of the oxygenates.

7.2   Needs

There are numerous areas of contaminant-removal research that need to be completed for MTBE and other oxygenates. One is to optimize GAC and air stripping technologies. For GAC and air stripping, work needs to be completed in developing a matrix of the effectiveness and cost of both treatments under various conditions. Also, some conditions may require both technologies for adequate removal. The air-stripping data need to be generated with and without off-gas control. This necessitates that the cost models for GAC and air stripping be brought up to date for comparison to other treatment technologies.

Other removal processes that need to be evaluated include abiotic oxidation, biodegradation, carbonaceous sorbents, reverse osmosis, SVE, and air sparging. As for abiotic

oxidation processes, Fenton's reagent (hydroxyl radicals) has been shown to be effective for MTBE. This process needs to be optimized so that a site demonstration can be conducted to determine its cost effectiveness. In addition, Fenton's reagent needs to be evaluated for other oxygenates, especially TBA, because this compound can also be a by-product from the biodegradation of MTBE. Other abiotic oxidation processes that need to be more extensively evaluated include ozone, ozone/peroxide, and ozone/UV. These processes have promise with regard to oxygenate destruction and are familiar treatment processes for drinking water.

Also, as mentioned previously, oxidation processes, such as ozonation, have been shown to increase the biodegradability of natural organics in the water. Therefore, the study of oxidation processes should also include the possibility of tandem biodegradation, because biofiltration may follow ozonation at drinking water treatment plants to control distribution system regrowth. Limited data exist for biodegradation under drinking water conditions, but the increase in biodegradability of natural organics due to ozone treatment potentially holds promise for the removal of oxygenates as a secondary substrate.

Optimal conditions for biodegradation processes for in situ and ex situ contaminant removal need to be determined. A particular focus should include the introduction of oxygen and nutrients for in situ plume treatment and the potential for abiotic oxidation and aerobic biodegradation porous-reactor barriers.

Carbonaceous sorbents, both natural and synthetic, are very effective in removing many types of organic compounds from water. Candidate natural sorbents may include vermiculite, straw, and peat. The sorption process is also very reversible for weakly sorbing contaminants such as MTBE under steam conditions. Therefore, a study of an automated system that would sorb MTBE then desorb (regenerate) under steam conditions should be initiated. An automated reverse osmosis system may be applicable for small utilities (under 500,000 gal/day). However, the potential for success of this process is limited due to the low molecular weights (32 to 102 Daltons) of most oxygenates, and thus only a quick, low-cost evaluation of this process is warranted.

The relative applicability of SVE for oxygenates other than MTBE also needs to be evaluated. The operating conditions and effectiveness of air sparging and of dual-phase extraction technology, currently used for gasoline, need to be investigated for MTBE and other oxygenates. For all technologies, comparative cost estimates are needed

8. EXPOSURE

8.1 Background

Based on limited monitoring/occurrence data (see above), the potential for exposure of biota and human populations to oxygenates would appear to be more than a hypothetical possibility. If the odor and taste of MTBE were as noxious for everyone as certain reports suggest it is for some persons (e.g., Angle, 1991; Vetrano, 1993a, b; TRC Environmental Corporation, 1993), few individuals would be likely to come into contact with MTBE in water long enough to allow significant exposure to occur. Taste and odor thresholds for MTBE have been reported as ranging from 39 to 135 µg/L for taste and 15 to 180 µg/L for odor (Young et al., 1996; Prah et al., 1994; Vetrano, 1993a,b; TRC Environmental Corporation, 1993). These measurements were obtained with small sets of subjects and cannot be considered representative of populations. Individuals and populations may vary considerably in sensitivity to, and tolerance of, odors and tastes, such that a given concentration of contaminant might be quite acceptable to a large majority of persons in one group and strongly rejected by an equal proportion in another. Thus, a population distribution of odor and taste thresholds for MTBE (as well as other oxygenates) may vary from one community to another. In the absence of statistically representative data on distributions of taste or odor tresholds, it cannot be assumed that the sensory properties of oxygenates would prevent all (or even most) people from ingesting such contaminants. Even if it were possible that all human exposure could be averted by treatment processes, exposure of biota to contaminated surface or groundwater could still occur.

Microenvironmental measurements of VOCs such as benzene and trichloroethylene in relation to household water usage (e.g., Lindstrom et al., 1994; Wilkes et al., 1996; McKone and Knezovich, 1991) point up the importance of considering multi-media, multi-route personal exposures. Note that "drinking water" is used in many ways besides direct ingestion, including food preparation (especially mixed in beverages and infant formula), dish washing, laundering, and bathing. In particular, showering affords a significant exposure potential by the inhalation and dermal routes, with variables such as water flow rate and temperature possibly influencing exposure levels (Giardino and Andelman, 1996). Although the volatility and other properties of oxygenates may differ from VOCs investigated thus far, the importance of microenvironmental

personal exposures in connection with contaminated household water usage would appear to apply to oxygenates as well.

8.2 Needs

At present, very little empirical information is available on either the overall distribution of exposures to oxygenates in water for the U.S. population as a whole or on selected "high-end" exposure scenarios where oxygenate contamination is already known to occur. One step toward determining the prevalence and level of potential exposures to oxygenates would be to obtain monitoring data from public water suppliers (see Section 2, above). However, establishing large-scale monitoring programs is probably not the most efficient or cost-effective means for characterizing the potential for human population exposures to oxygenates. Rather, statistically representative sampling of public and private water supplies may afford a more cost-effective approach. By coupling such data with qualitative and quantitative data on water usage and consumption patterns, it should be possible to model human exposures to specified oxygenates for risk assessment purposes (cf. Brown, 1997).

With respect to locales where oxygenate contamination of the public water supply has already been documented, the focus should be on evaluating potential personal exposure scenarios involving all household uses of oxygenate-contaminated water (e.g., for drinking, food preparation, cleaning, bathing). Several studies of multi-route VOC exposures through showering and other uses of tap water (e.g., Weisel and Jo, 1996) provide a substantial foundation for modeling as well as empirical studies of oxygenate exposure. As a first step, modeling of personal exposures, possibly using integrative approaches that incorporate macro- and micro-environmental pathways and even pharmacokinetic aspects (Georgopoulos et al., 1997; Piver et al., 1997), should be undertaken, using sensitivity analyses to identify areas of needed additional data. If exposures appear to be of concern, biomarkers of exposure (e.g., protein/DNA adducts, metabolites such as TBA) should be evaluated.

More extensive data on odor and taste thresholds and hedonics are also needed to determine whether or how exposures may be affected by sensory variables. Note that detection and recognition thresholds for taste and odor sensations are distinct from their hedonic properties, which involve dimensions such as the (un)pleasantness and intensity of the sensory experience. Hedonic reactions may figure importantly, along with considerations of consumer cost,

convenience, and other factors, in the levels of contamination that individuals or communities will reject or accept (and consequently be exposed to) in their drinking water. Also, cognitive factors, including attitudes that may be shaped by information provided through the social milieu, may significantly influence sensory perception (Dalton, 1996). Consequently, further research in this area should be undertaken with appropriate methods to deal with these complex confounding variables. The separate issue of what contaminant level is acceptable from an aesthetic standpoint is a policy matter for community public water suppliers or other geopolitical units to determine, and should not be confused with an exposure assessment question.

9.   AQUATIC TOXICITY

9.1   Background

The aquatic toxicity of oxygenates has been briefly summarized in the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). Toxicity data (LC-50 or EC-50 values) exist for MTBE, ETBE, TAME, DIPE, EtOH, and TBA for selected aquatic species (e.g., *Daphnia magna*, *Pimephales promelas*, *Carassius auratus*). However, EPA has not established water quality criteria for oxygenates for the protection of freshwater or marine aquatic life. API has recently completed a search and evaluation of the extant literature on the acute and chronic toxicity of oxygenates for aquatic organisms and has provided the results of that search to EPA. From the data gaps identified through that effort, testing to fill critical needs is expected to be conducted within a year of the API submission. EPA's Office of Water may then decide to prepare Water Quality Criteria for oxygenates.

9.2   Needs

Current actions should provide an appropriate basis for later determining whether additional effects testing or research is needed.

10. HEALTH EFFECTS

10.1 Background

Most of the testing and research on the toxicity of oxygenates has been concerned with the effects of *inhaled* MTBE in laboratory animals and human volunteers. Virtually no information exists on the effects of *ingested* oxygenates on humans, with the notable exception of the extensive database on the health effects of ingested ethanol. However, absent any evidence indicating that human populations are exposed to ethanol-contaminated drinking water, the well characterized health effects of ingested ethanol need not be considered here.

Few studies exist on the acute and subacute (e.g., Robinson et al., 1990; IIT Research Institute, 1992) or chronic (Belpoggi et al., 1995) toxicity of MTBE in laboratory animals via oral exposure. Since 1992 when the EPA Office of Water released a draft Health Advisory of 20-200 μg/L for MTBE in drinking water, only a carcinogenicity study by Belpoggi et al. (1995) has been published, and this study was alluded to in the 1992 draft Health Advisory as a basis for identifying 20 μg/L as a guidance level. The lack of a more substantial health effects database has made it difficult to develop a final Health Advisory or derive an oral Reference Dose (RfD) for MTBE. Questions have been raised (e.g., by the National Research Council, 1996) about the use of some of these studies for risk assessment purposes. At a minimum, the use of olive oil as a vehicle for administering MTBE to rats in the chronic bioassay by (Belpoggi et al. (1995) may be problematic with respect to assessing the health risks of MTBE in drinking water.

Oral toxicity data for other ethers are even more limited in availability, although some work on inhaled vapors of ETBE and TAME is currently being conducted under provisions of a TSCA Enforceable Consent Agreement (Federal Register, 1995). Ingested TBA has been evaluated in rats and mice in a chronic bioassay by National Toxicology Program (Cirvello et al., 1995).

10.2 Needs

Given the limitations of available information on the oral toxicity of MTBE and the much greater database on the inhalation toxicity of MTBE, the question arises as to whether more oral toxicity studies should be initiated, or should inhalation toxicity data be extrapolated to estimate oral toxicity risk. A significant effort is already being devoted to developing a physiologically

based pharmacokinetic (PBPK) model for MTBE in rodents to support human health risk assessment (Borghoff et al., 1996). Although the model appears to accurately predict blood levels of MTBE and metabolites such as TBA at low inhalation exposure levels of MTBE, it does not yet predict TBA levels accurately in target tissues other than blood in rodents. If the model is to provide a basis for extrapolating from inhalation effects to oral toxicity, it must be able to predict TBA levels in target organs such as the kidney. Moreover, it must be adequate for extrapolation from rodents to humans. A pharmacokinetic study of human volunteers exposed to MTBE by inhalation and oral routes is planned by EPA's Office of Research and Development. These various efforts need to be pursued in the near-term until an adequate PBPK model exists to accurately predict levels of MTBE and metabolites such as TBA and possibly formaldehyde (HCHO) in rodent and human target organs, particularly under low-level exposure conditions.

The options of initiating further oral toxicity studies or of using PBPK modeling to support an extrapolation from inhalation effects to oral toxicity risk are not necessarily an "either/or" situation. Strategically, it may be advisable to conduct another study of subchronic oral exposure to MTBE to investigate the potential for toxic effects as well as to help validate a PBPK model for cross-route extrapolation. If the PBPK modeling effort should turn out not to be able to support such an extrapolation with reasonable confidence, then a new chronic bioassay would be advisable to reduce the uncertainties in assessing human health risks from chronic exposure to MTBE in drinking water.

Questions about the relevance of tumors observed in laboratory rodents exposed to high concentrations of MTBE by inhalation (Bird et al., 1997) and oral (Belpoggi et al., 1995) routes also need to be resolved if uncertainties in current assessments of human cancer risk are to be reduced. In view of the weight necessarily attached to the few cancer bioassays on MTBE, it would be desirable to reexamine and confirm the pathology data from all of these studies (Bird et al., 1997; Belpoggi et al., 1995). Alternative assays for carcinogenicity, such as transgenic mice (Tennant et al., 1995) and Medaka fish (Boorman et al., 1997) assays, could offer relatively rapid approaches for collecting additional data that could contribute to a weight-of-evidence determination as well as potentially shed light on modes of action. Although the latter approaches are unlikely to provide dose-response information that would enhance quantitative potency estimation, which is a critical need, and interpretation of negative results from these assays could be problematic, nevertheless they could provide supporting or confirmative

evidence of certain tumor types and thus assist in interpreting the relevance of inhalation effects for drinking water exposure.

The database for TBA may be adequate to characterize the toxicity of TBA. Given the unknown but conceivable potential for human exposure to TBA either as a metabolite, as an oxygenate itself, or as a natural biodegradation product of MTBE in groundwater, an assessment of the carcinogenic and noncarcinogenic health risks of TBA should be undertaken.

The best strategy for the other ethers may be to obtain pharmacokinetic data, some of which work is already underway for the inhalation route, and take such information into account in designing and conducting oral toxicity testing of these ethers. This strategy is predicated on low usage of ethers other than MTBE. If occurrence or exposure data become available and suggest otherwise, the need for more intensive investigation of the pharmacokinetics and health effects of other ethers may be elevated. As for degradation products of oxygenates (other than TBA), more information on the occurrence and concentrations of these chemicals is needed to guide decision-making about which chemicals to test.

11.   CONCLUSIONS

Certain priorities emerge from the foregoing discussion. Without attempting to place them in rank order, the following set of needed studies should be given priority consideration:

- Inclusion of oxygenate analytes and principal suspected transformation products wherever VOC monitoring of water is routinely performed
- Determination of the relative contributions of point and non-point sources of oxygenate fluxes to surface and groundwaters
- More extensive evaluation of oxygenate effects on materials used in tanks and pipelines, especially after aging over a period of years
- Determination of oxygenate biodegradation rates and pathways under representative geochemical conditions, and identification of degradation by-products and their environmental fate
- Evaluation of the relative cost-effectiveness of candidate technologies for removing oxygenate contaminants from water under various conditions, with iterative efforts to optimize the most

promising technologies, develop new innovative approaches, and evaluate the comparative cost effectiveness of available technologies

- Statistically representative sampling of public water supplies and modeling of multi-media, multi-pathway personal exposures for estimating population distributions of exposures; modeling and empirical studies of "high-end" microenvironmental exposure scenarios
- Completion of PBPK modeling and cancer mechanistic studies to enhance confidence in extrapolating from laboratory animal inhalation toxicity data as a basis for estimating oral toxicity risk of MTBE for humans; subchronic oral toxicity study of MTBE in drinking water
- Updating of risk characterizations as results of the above work become available

REFERENCES

Alexander, J. E.; Ferber, E. P.; Stahl, W. M. (1994) Avoid leaks from reformulated fuels: choose an elastomeric sealing material according to the type and concentration of oxygenate (ether and/or alcohol) added to the fuel. Fuel Reformulation 4(Mar/Apr): 42-46.

American Petroleum Institute. (1994) Effects of oxygenated fuels and reformulated diesel fuels on elastomers and polymers in pipeline/terminal components. Washington, DC: American Petroleum Institute; API publication 1132.

Angle, C. R. (1991) If the tap water smells foul, think MTBE [letter]. JAMA J. Am. Med. Assoc. 266: 2985-2986.

Anonymous. (1996) MTBE contamination forces well closures. Groundwater Newsl. 25(16): 1.

Baehr, A. L.; Ayers, M. A. (1997) Occurrence and movement of contaminants through the urban hydrologic cycle—FY97 workplan update [for NAWQA Comprehensive Urban Study]. West Trenton, NJ: U.S. Geological Survey, Long Island-New Jersey National Water-Quality Assessment Program; February 1.

Belpoggi, F.; Soffritti, M.; Maltoni, C. (1995) Methyl-tertiary-butyl ether (MTBE)—a gasoline additive—causes testicular and lymphohaematopoeitic cancers in rats. Toxicol. Ind. Health 11: 119-149.

Benson, D. (1994) VENT2D, Ver. 1.3. Reno, NV.

Bird, M. G.; Burleigh-Flayer, H. D.; Chun, J. S.; Douglas, J. F.; Kneiss, J. J.; Andrews, L. S. (1997) Oncogenicity studies of inhaled methyl tertiary-butyl ether (MTBE) in CD-1 mice and F-344 rats. J. Appl. Toxicol. 17(suppl. 1): S45-S55.

Boorman, G. A.; Botts, S.; Bunton, T. E.; Fournie, J. W.; Harshbarger, J. C.; Hawkins, W. E.; Hinton, D. E.; Jokinen, M. P.; Okihiro, M. S.; Wolfe, M. J. (1997) Diagnostic criteria for degenerative, inflammatory, proliferative nonneoplastic and neoplastic liver lesions in medaka (*Oryzias latipes*): consensus of a national toxicology program pathology working group. Toxicol. Pathol. 25: 202-210.

Borden, R. C.; Daniel, R. A.; LeBrun, L. E., IV; Davis, C. W. (1997) Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer. Water Resour. Res. 33: 1105-1115.

Borghoff, S. J.; Murphy, J. E.; Medinsky, M. A. (1996) Development of a physiologically based pharmacokinetic model for methyl *tertiary*-butyl ether and *tertiary*-butanol in male Fischer-344 rats. Fundam. Appl. Toxicol. 30: 264-275.

Brown, S. L. (1997) Atmospheric and potable water exposures to methyl tert-butyl ether (MTBE). Regul. Toxicol. Pharmacol. 25: 256-276.

California Department of Health Services. (1997) Summary of sampling of public drinking water systems for methyl tertiary butyl ether (MTBE): covers data through July 14. Sacramento, CA: Prevention Services, Division of Drinking Water and Environmental Management; http//www.dhs.cahwnet.gov/prevsrv/ddwem/MTBE.htm.

Chen, C. T.; Tafuri, A. N.; Rahman, M.; Foerst, M. B.; Pfetzing, E.; Taylor, M. (1995) Oxidation of methyl-t-butyl ether (MTBE) using Fenton's Reagent. In: Proceedings of the 88th annual meeting of the Air & Waste Management Association; June; San Antonio, TX; paper no. 95-WA91.03.

Cho, J. S.; Wilson, J. T.; DiGiulio, D. C.; Vardy, J. A.; Choi, W. (1997) Implementation of natural attenuation at a JP-4 jet fuel release after active remediation. Biodegradation: accepted.

Cirvello, J. D.; Radovsky, A.; Heath, J. E.; Farnell, D. R.; Lindamood, C., III. (1995) Toxicity and carcinogenicity of *t*-butyl alcohol in rats and mice following chronic exposure in drinking water. Toxicol. Ind. Health 11: 151-165.

Cowan, R. M.; Park, K. (1996) Biodegradation of the gasoline oxygenates MTBE, ETBE, TAME, TBA, and TAA by aerobic mixed culture. In: Proceedings of the 28th mid-Atlantic industrial and hazardous waste conference; Buffalo, NY; pp. 523-530.

Dale, M. S.; Losee, R. F.; Crofts, E. W.; Davis, M. K. (1997) MTBE: occurrence and fate in source-water supplies. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 376-377.

Dalton, P. (1996) Odor perception and beliefs about risks. Chem. Senses 21: 447-458.

Delzer, G. C.; Zogorski, J. S.; Lopes, T. J.; Bosshart, R. L. (1996) Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991-95. Rapid City, SD: U.S. Geological Survey; water-resources investigations report 96-4145.

Federal Register. (1995) Testing consent order for tertiary amyl methyl ether. F. R. (March 21) 54: 14910-14912.

Garrett, P. (1987) Oxygenates as ground water contaminants. Presented at: 1987 conference on alcohols and octane; April; San Antonio, TX.

Georgopoulos, P. G.; Walia, A.; Roy, A.; Lioy, P. J. (1997) Integrated exposure and dose modeling and analysis system. 1. Formulation and testing of microenvironmental and pharmacokinetic compounds. Environ. Sci. Technol. 31: 17-27.

Giardino, N. J.; Andelman, J. B. (1996) Characterization of the emissions of trichloroethylene, chloroform, and 1,2-dibromo-3-chloropropane in a full-size, experimental shower. J. Exposure Anal. Environ. Epidemiol. 6: 413-423.

Grady, S. J. (1997) Distribution of MTBE in ground water in New England by aquifer type and land use. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 392-394.

Health Effects Institute. (1996) The potential health effects of oxygenates added to gasoline: a review of the current literature, a special report of the Institute's Oxygenates Evaluation Committee. Cambridge, MA: Health Effects Institute, Oxygenates Evaluation Committee.

IIT Research Institute. (1992) Twenty-eight day oral (gavage) toxicity study of methyl *tert*-butyl ether (MTBE) in rats [final report]. Chicago, IL: IIT Research Institute; project no. L08100SN1602.

Interagency Oxygenated Fuels Assessment Steering Committee. (1996) Interagency assessment of potential health risks associated with oxygenated gasoline. Washington, DC: National Science and Technology Council; Office of Science and Technology Policy.

Interagency Oxygenated Fuels Assessment Steering Committee. (1997) Interagency assessment of oxygenated fuels. Washington, DC: National Science and Technology Council, Office of Science and Technology Policy.

Lindsey, B. D.; Breen, K. J.; Daly, M. H. (1997) MTBE in water from fractured-bedrock aquifers, southcentral Pennsylvania. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 399-400.

Lindstrom, A. B.; Highsmith, V. R.; Buckley, T. J.; Pate, W. J.; Michael, L. C. (1994) Gasoline-contaminated ground water as a source of residential benzene exposure: a case study. J. Exposure Anal. Environ. Epidemiol. 4: 183-195.

McKinnon, R. J.; Dyksen, J. E. (1984) Removing organics from groundwater through aeration plus GAC. J. Am. Water Works Assoc. 76: 42- 47.

McKone, T. E.; Knezovich, J. P. (1991) The transfer of trichloroethylene (TCE) from a shower to indoor air: experimental measurements and their implications. J. Air Waste Manage. Assoc. 41: 832-837.

Mo, K.; Lora, C.; Javanmardian, M.; Yang, X.; Kulpa, C. F. (1996) Biodegradation of gasoline oxygenate, methyl-t-butyl ether by mixed and pure culture. In: Abstracts of the 96th general meeting of the American Society of Microbiology. Washington, DC: American Society of Microbiology; abstract no. Q-298, p. 437.

Mormile, M. R.; Liu, S.; Suflita, J. M. (1994) Anaerobic biodegradation of gasoline oxygenates: extrapolation of information to multiple sites and redox conditions. Environ. Sci. Technol. 28: 1727-1732.

National Research Council; Committee on Toxicological and Performance Aspects of Oxygenated and Reformulated Motor Vehicle Fuels. (1996) Toxicological and performance aspects of oxygenated motor vehicle fuels. Washington, DC: National Academy Press.

Pankow, J. F.; Thomson, N. R.; Johnson, R. L.; Baehr, A. L.; Zogorski, J. S. (1997) The urban atmosphere as a non-point source for the transport of MTBE and other volatile organic compounds (VOCs) to shallow groundwater. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 385-387.

Petroleum Environmental Research Forum. (1993) Aerobic biodegradation of MTBE - basic fate of biokinetics evaluation, final report of PERF project 90-10, June, 1993.

Piver, W. T.; Jacobs, T. L.; Medina, M. A., Jr. (1997) Evaluation of health risks for contaminated aquifers. Environ. Health Perspect. 105(suppl. 1): 127-143.

Prah, J. D.; Goldstein, G. M.; Devlin, R.; Otto, D.; Ashley, D.; House, D.; Cohen, K. L.; Gerrity, T. (1994) Sensory, symptomatic, inflammatory, and ocular responses to and the metabolism of methyl tertiary butyl ether in a controlled human exposure experiment. Inhalation Toxicol. 6: 521-538.

Robinson, M.; Bruner, R. H.; Olson, G. R. (1990) Fourteen- and ninety-day oral toxicity studies of methyl tertiary-butyl ether in Sprague-Dawley rats. J. Am. Coll. Toxicol. 9: 525-540.

Salanitro, J. P.; Diaz, L. A.; Williams, M. P.; Wisniewski, H. L. (1994) Isolation of a bacterial culture that degrades methyl *t*-butyl ether. Appl. Environ. Microbiol. 60: 2593-2596.

Salanitro, J. P.; Diaz, L. A.; Williams, M. P.; Wisniewski, H. L. (1995) Erratum: Isolation of a bacterial culture that degrades methyl-*t*-butyl ether. Appl. Environ. Microbiol. 61: 406.

Schwartz, D. A. (1997) MTBE case casts doubt on letting LUST sites be. Bio-Cleanup Rep. (March 1): 5.

Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; McIver, C. D.; Bufalini, J. J. (1991) The photooxidation of methyl *tertiary* butyl ether. Int. J. Chem. Kinet. 23: 907-924.

Speth, T. F.; Miltner, R. J. (1990) Technical note: adsorption capacity of GAC for synthetic organics. J. Am. Water Works Assoc. 82: 72-75.

Squillace, P. J.; Zogorski, J. S.; Wilber, W. G.; Price, C. V. (1996) Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1994. Environ. Sci. Technol. 30: 1721-1730.

Stackelberg, P. E.; O'Brien, A. K.; Terracciano, S. A. (1997) Occurrence of MTBE in surface and ground water, Long Island, New York, and New Jersey. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 394-397.

Suflita, J. M.; Mormile, M. R. (1993) Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface. Environ. Sci. Technol. 27: 976-978.

Tennant, R. W.; French, J. E.; Spalding, J. W. (1995) Identifying chemical carcinogens and assessing potential risk in short-term bioassays using transgenic mouse models. Environ. Health Perspect. 103: 942-950.

TRC Environmental Corporation. (1993) Odor threshold studies performed with gasoline and gasoline combined with MTBE, ETBE and TAME. Washington, DC: American Petroleum Institute; API publication no. 4592.

Truong, K. N.; Parmele, C. S. (1992) Cost-effective alternative treatment technologies for reducing the concentrations of methyl tertiary butyl ether and methanol in groundwater. In: Calabrese, E. J.; Kostecki, P. T., eds. Hydrocarbon contaminated soils and groundwater: v. 2. Boca Raton, Fl: Lewis Publishers; pp. 461-486.

U.S. Department of Energy. (1995a) Imports of crude oil and petroleum products by PAD district, 1995 [data from form EIA-841, monthly imports report]. In: Petroleum supply annual 1995: volume 1. Washington, DC: Energy Information Administration, Office of Oil & Gas; p. 55; report no. DOE/EIA-0340(95).

U.S. Department of Energy. (1995b) Monthly oxygenate telephone report: form EIA-819M. In: Petroleum supply monthly: December. Washington, DC: Energy Information Administration, Office of Oil & Gas; p. 135; report no. DOE/EIA-0109(95/12).

U.S. Environmental Protection Agency. (1992) Measurement of purgeable organic compounds in water by capillary-column gas chromatography/mass spectrometry, method 524.2, revision 4.0. Cincinnati, OH: Environmental Monitoring Systems Laboratory; August.

U.S. Environmental Protection Agency. (1993) Assessment of potential risks of gasoline oxygenated with methyl tertiary butyl ether (MTBE). Washington, DC: Office of Research and Development; November; report no. EPA/600/R-93/206.

U.S. Environmental Protection Agency. (1994) Health risk perspectives on fuel oxygenates. Washington, DC: Office of Research and Development; report no. EPA 600/R-94/217.

U.S. Environmental Protection Agency. (1996) Oxyfuels information needs. Research Triangle Park, NC: National Center for Environmental Assessment; report no. EPA/600/R-96/069. Available from: NTIS, Springfield, VA; PB96-190665REB.

U.S. Environmental Protection Agency. (1997) Options for the National Drinking Water Contaminant Occurrence Data Base: background document (working draft) for the National Contaminant Occurrence Data Base stakeholders meeting May 21-22, 1997, Washington, D.C. Washington, DC: U.S. Environmental Protection Agency, Office of Water; pp. 10-14; report no. EPA 815-D-97-001.

Vetrano, K. (1993a) Odor and taste threshold studies performed with tertiary-amyl methyl ether (TAME). Washington, DC: American Petroleum Institute; API publication no. 4591.

Vetrano, K. M. (1993b) Final report to ARCO Chemical Company on the odor and taste threshold studies performed with methyl tertiary-butyl ether (MTBE) and ethyl tertiary-butyl ether (ETBE). Windsor, CT: TRC Environmental Corporation; project no. 13442-M31.

Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. (1988) Gas-phase reactions of hydroxyl radicals with the fuel additives methyl *tert*-butyl ether and *tert*-butyl alcohol over the temperature range 240-440 K. Environ. Sci. Technol. 22: 842-844.

Weisel, C. P.; Jo, W.-K. (1996) Ingestion, inhalation, and dermal exposures to chloroform and trichloroethene from tap water. Environ. Health Perspect.104: 48-51.

Westbrook, P. A.; French, R. N. (1995) Considerations on the use of nonmetallic materials in oxygenated fuel emvironments. Presented at: O&E symposium materials/fuels compatibility workshop; September. Washington, DC: American Petroleum Institute.

Wilkes, C. R.; Small, M. J.; Davidson, C. I.; Andelman, J. B. (1996) Modeling the effects of water usage and co-behavior on inhalation exposures to contaminants volatilized from household water. J. Exposure Anal. Environ. Epidemiol. 6: 393-412.

Wilson, B. Unpublished data.

Wyborny, L. A., II. (1997) Oxy-water res strategy question -reply [email memorandum to J. Michael Davis, U.S. EPA, RTP, NC]. Ann Arbor, MI: U.S. Environmental Protection Agency, Office of Mobile Sources; August 18.

Yeh, K.-J. (1992) Degradation of gasoline oxygenates in the subsurface. Blacksburg, VA: Virginia Polytechnic Institute.

Young, W. F.; Horth, H.; Crane, R.; Ogden, T.; Arnott, M. (1996) Taste and odour threshold concentrations of potential potable water contaminants. Water Res. 30: 331-340.

APPENDIX 1

CHEMICAL PROPERTIES OF SELECTED OXYGENATES

Chemical Name	Methyl Tert-Butyl Ether	Ethyl Tert-Butyl Ether	Tert-Amyl Methyl Ether	Diisopropyl Ether
CAS Registry No.	1634-04-4	637-92-3	994-05-8	108-20-3
Synonyms	MTBE; 2-methyl, 2-methoxy propane; tert-butyl methyl ether; methyl tertiary butyl ether; methyl-tert-butyl ether	ETBE; tert-butyl ethyl ether; propane, 2-ethoxy-2methyl; 1, 1-dimethyl ethyl ether	TAME; 2-methoxy-2 methylbutane; methyl tert-pentyl ether; 1,1-dimethylpropyl methyl ether; methyl tert-amyl ether	DIPE; 2'2-oxybispropane; 2-isopropoxy-propane
Molecular Weight (g/mol)	88.15	102.18	102.18	102.18
Molecular Formula	$C_5H_{12}O$	$C_6H_{14}O$	$C_6H_{14}O$	$C_6H_{14}O$
Structural Formula	$CH_3OC(CH_3)_3$	$(CH_3)_3COCH_2CH_3$	$CH_3CH_2C(CH_3)_2OCH_3$	$(CH_3)_2CHOCH(CH_3)_2$
Boiling Point[a]	55.2 °C	72.2 °C	86.3 °C	68.2 °C
Vapor Pressure[b] (mm Hg)	240	130	75	159
Vapor Density[d]	3.1	3.6	3.6	3.6
Density (g/ml at 20 °C)	0.74	0.74	0.77	0.73
Solubility (g/100 g water)	4.8	1.2	1.2	0.2
Henry's Law Constant				
(Atm-m^3)/ (g- mole)	5.28E-4 to 3E-3	2.64E-3	1.95E-3	4.77E-3
Dimensionless	2.2E-2 to 1.2E-1	0.11	0.081	0.199
Log K_{oc}	0.55 to 0.91	NA	NA	1.13
Log K_{ow}	0.94 to 1.30	NA	NA	1.52

Chemical Name	Tert-Amyl Ethyl Ether	Methane, Oxybis	Tert-Butyl Alcohol	Ethanol
CAS Registry No.	919-94-8	115-10-6	75-65-0	64-17-5
Synonyms	TAEE; ethyl tert-amyl ether; butane, 2-ethoxy-2-methyl	DME; dimethyl ether	TBA; 2-propanol, 2-methyl	ethyl alcohol
Molecular Weight (g/mol)	116.20	46.07	74.12	46.07
Molecular Formula	$C_7H_{16}O$	C_2H_6O	$C_4H_{10}O$	C_2H_6O
Structural Formula	$CH_3CH_2C(CH_3)_2OCH_2CH_3$	CH_3OCH_3	$(CH_3)_3COH$	CH_3CH_2OH
Boiling Point[a]	102 °C	−24.8 °C	82.4 °C	78.5 °C
Vapor Pressure[b] (mm Hg)	NA	758 to 5086[c]	41	44
Vapor Density[d]	4.0	1.6	2.6	1.6
Density (g/ml)	0.75	0.66	0.79	0.79
Solubility in Water (g/100 g water)	NA	4.7 to 35.3	miscible	miscible
Henry's Law Constant				
$(Atm-m^3)/$ (g-mole)	NA	4.89E-4 to 9.97E-4	1.21E-5	6.91E-6
Dimensionless	NA	2.03E-2 to 4.15E-2	5.03E-4	2.83E-4
Log K_{oc}	NA	-0.29	1.57	-0.14
Log K_{ow}	NA	0.10	0.35	-0.32

[a]At 760 mm Hg.
[b]At 20 °C.
[c]At 25°C
[d]Air = 1.